

Long-Term Effects of Nitrogen Fertilizer Use on Ground Water Nitrate in Two Small Watersheds

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ABSTRACT

Changes in agricultural management can minimize $\text{NO}_3\text{-N}$ leaching, but then the time needed to improve ground water quality is uncertain. A study was conducted in two first-order watersheds (30 and 34 ha) in Iowa's Loess Hills. Both were managed in continuous corn (*Zea mays* L.) from 1964 through 1995 with similar N fertilizer applications (average $178 \text{ kg ha}^{-1} \text{ yr}^{-1}$), except one received applications averaging $446 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ between 1969 and 1974. This study determined if $\text{NO}_3\text{-N}$ from these large applications could persist in ground water and baseflow, and affect comparison between new crop rotations implemented in 1996. Piezometer nests were installed and deep cores collected in 1996, then ground water levels and $\text{NO}_3\text{-N}$ concentrations were monitored. Tritium and stable isotopes (^2H , ^{18}O) were determined on 33 water samples in 2001. Baseflow from the heavily N-fertilized watershed had larger average $\text{NO}_3\text{-N}$ concentrations, by 8 mg L^{-1} . Time-of-travel calculations and tritium data showed ground water resides in these watersheds for decades. "Bomb-peak" precipitation (1963–1980) most influenced tritium concentrations near lower slope positions, while deep ground water was dominantly pre-1953 precipitation. Near the stream, greater recharge and mixed-age ground water was suggested by stable isotope and tritium data, respectively. Using sediment-core data collected from the deep unsaturated zone between 1972 and 1996, the increasing depth of a $\text{NO}_3\text{-N}$ pulse was related to cumulative baseflow ($r^2 = 0.98$), suggesting slow downward movement of $\text{NO}_3\text{-N}$ since the first experiment. Management changes implemented in 1996 will take years to fully influence ground water $\text{NO}_3\text{-N}$. Determining ground water quality responses to new agricultural practices may take decades in some watersheds.

AGRICULTURAL LAND USE has frequently been associated with loadings of nutrients to ground and surface waters (Burkart and Stoner, 2001; Castillo et al., 2000; Sauer et al., 2001; Schilling and Libra, 2000.) It is also widely reported that agricultural practices can be modified to reduce these loadings through nutrient management (Kitchen and Goulding, 2001), crop rotation (Bolton et al., 1970; Owens et al., 1995; Randall et al., 1997), and the use of biological filters (e.g., Peterjohn and Correll, 1983; Nelson et al., 1995; Spruill, 2000; Gold et al., 2001). Once a change in an agricultural system is implemented, there may be rapid improvement in the quality of runoff waters if those changes increase infiltration and reduce sediment transport. But in the humid Midwestern USA, most streamflow is typically dominated by baseflow that originates from ground water. The timing of ground water quality responses to changes in agricultural management is not readily predicted and depends on the size of the area being monitored, depths

to saturation, the thickness of the saturated media, velocity and directions of ground water movement, and the type and spatial extent of management changes that are implemented.

Ground water quality in agricultural areas of the Midwest has been particularly affected by $\text{NO}_3\text{-N}$ leaching (Burkart and Stoner, 2001). Changes in cropping practices including multicrop rotations and N fertilizer management may help reduce this contamination, but the changes in ground water quality may substantially lag changes in management. Underestimating the time required for water quality improvement could cause incorrect assessments of the effect of new practices on water quality, if the assessments are based on short-term studies. The potential lag in water quality response also has implications for the setting of realistic timelines to achieve targeted water quality improvements in watersheds. Unfortunately, documenting the timing of water quality responses to new management practices has received little attention, and there are few reports of watershed- or landscape-scale changes in ground water quality resulting from specific changes in agricultural management.

Long-term studies under documented management are needed to develop knowledge on the timing of ground water quality response to new practices. Opportunities to examine these responses with field data should be identified and exploited. This paper presents a comparison between two small watersheds (30 and 34 ha) for which there is nearly a 40-year record of management history and stream flow. The hydrology and geology of these two adjacent watersheds are essentially identical. Agricultural management practices were also identical, except for two periods between 1969 and 1974, and from 1996 until present. Both of these experimental periods were hypothesized to cause a difference in $\text{NO}_3\text{-N}$ concentrations in ground water and stream baseflow between the two catchments. Could an experimental effect from the first treatment period possibly persist and confound a comparison between the current experimental practices? The objective of this study was to determine if any current differences in $\text{NO}_3\text{-N}$ concentrations could, at least in part, be attributed to a residual effect from the 1969–1974 experiment.

This study included several techniques that included estimating the travel time of ground water through the watershed with physical and isotopic methods. Isotopes of water (^{18}O , ^2H , and ^3H) have often been used to help interpret hydrologic systems, both surface water (Genereux and Hooper, 1998) and ground water (Gonfiantini et al., 1998). Changes in stable isotope (^{18}O , ^2H) composition occur due to changes in water phase (evap-

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Abbreviations: K_s , saturated hydraulic conductivity; TU, tritium units.

oration, sublimation, condensation) in the atmosphere (Ingraham, 1998), at the land surface (Walker and Krabbenhoft, 1998), and in the shallow subsurface (Barnes and Turner, 1998). Spatial and temporal changes in isotopic composition can be used to determine relative water sources and dominant hydrologic processes, and thus aid interpretation of storm flow pathways (Buttle and Sami, 1990; DeWalle et al., 1997; Genereux and Hooper, 1998), ground water flow (Gonfiantini et al., 1998; Hendry, 1988; Kehew et al., 1998; Matheney and Gerla, 1996), and plant water use (Burgess et al., 2000; Dawson and Ehleringer, 1998).

Tritium (^3H) is an unstable isotope, with a half-life of 12.43 years, that increased in the atmosphere and in precipitation following aboveground testing of nuclear weapons during the late 1950s and early 1960s, then decreased rapidly after 1963 after testing was banned (Ingraham, 1998). This pulse of tritiated waters has allowed relative aging of ground water, essentially into three classes: "pre-bomb" (before 1953), "bomb-peak" (from the mid 1950s to the late 1970s or early 1980s), and more recent waters (after about 1980). These three age classes are relevant to this study given the dating of the two experiments. Discerning these relative ages is becoming difficult as isotopic decay of "bomb" tritium proceeds. Further discussion and case studies are provided by Bradbury (1991), Daniels et al. (1991), Gonfiantini et al. (1998), and Ingraham (1998).

Nitrogen isotopes ($^{15}\text{N}/^{14}\text{N}$) of natural abundance have also been used in environmental studies; however, diagnostic use is typically restricted to distinguishing animal- (and/or human-) waste sources from soil organic matter (SOM) or fertilizer sources (e.g., Spalding et al., 1982; Kendall, 1998). Soil organic matter and fertilizer sources can become difficult to distinguish in ground water because their ranges of isotopic ratios overlap, soil N-cycle processes (i.e., immobilization, mineralization) in time mix soil and fertilizer-applied N, and $\text{NO}_3\text{-N}$ in deep soils and ground water could be subject to denitrification, which results in ^{15}N enrichment of residual $\text{NO}_3\text{-N}$ (Kendall, 1998). The two watersheds in this study never received manure applications, and the only known sources of $\text{NO}_3\text{-N}$ are SOM and applied fertilizer. Therefore, natural abundance N isotopes would not be expected to answer the question being asked in this study.

Nitrate originating from geologic parent materials can occur, but these have only been reported as important sources in more arid areas to the west. Boyce et al. (1976) reported that $\text{NO}_3\text{-N}$ concentrations in Nebraska loess were diminished in eastern portions of that state's deep-loess region. Regardless, any geologic source for the $\text{NO}_3\text{-N}$ should not cause a difference in $\text{NO}_3\text{-N}$ concentrations between these two watersheds, which border one another and have virtually identical geology, pedology, and hydrology. The duration of cultivation is also believed to be similar. Both watersheds were probably cultivated since about 1880, based on Potawatamie County records of cropland acreage (Larry Kramer, personal communication, 2002).

In this paper, the hydrology, water-isotope chemistry,

and $\text{NO}_3\text{-N}$ concentrations of ground water and unsaturated sediments are compared between two adjacent first-order watersheds in the Loess Hills of southwestern Iowa. Hydraulic and isotopic data are used to evaluate the subsurface flow system. It is hypothesized that isotopic signatures will help interpret relative ages and pathways of ground water in the two small watersheds at this southwestern Iowa site. If both the physical and the isotopic methods indicate that rainfall predating 1980 still resides within ground water of these watersheds, then any differences in $\text{NO}_3\text{-N}$ concentrations between these two watersheds could result, at least in part, from the 1969–1974 experiment. The $\text{NO}_3\text{-N}$ concentrations themselves were also evaluated and compared with historical data to provide an additional line of evidence for evaluating the possible persistence of $\text{NO}_3\text{-N}$ from the first experiment.

SETTING AND BACKGROUND

The study took place within Watersheds 1 and 2 of the Deep Loess Research Station (DLRS), located 10 km south of Treynor, Iowa (Fig. 1). The station was established to carry out research on agricultural hydrology and has a research history dating back to the mid-1960s, with much of the research focused on erosion and nutrient balances under corn production (e.g., Karlen et al., 1998, 1999; Logsdon et al., 1999). Soils developed in the deep loess are dominantly mapped as Monona (Typic Hapludolls), Ida (Typic Udorthents), Napier, and Kennebec (both Cumulic Hapludolls) soils (Soil Survey Staff, 1994), and more than a third of the area is highly eroded (Karlen et al., 1999).

Both watersheds were under a continuous corn rotation with a conventional tillage system from 1964 through 1995 (Table 1) and have shown similar runoff and baseflow volumes (Kramer et al., 1999). There was an experimental change in nitrogen fertilizer applications between 1969 and 1974, when Watershed 1 received an average of $446 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and Watershed 2 received an average of $172 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Table 1). These applications were made in spring mostly as anhydrous ammonia, but some of the increased N in Watershed 1 was applied as granular NH_4NO_3 (Burwell et al., 1976). This experiment was used to assess $\text{NO}_3\text{-N}$ movement in deep soils (Schuman et al., 1975; Alberts et al., 1977) and its export in baseflow (Burwell et al., 1976, 1977). However, total losses of N via stream discharge during the six-year experiment only showed a 111 kg ha^{-1} difference between Watersheds 1 and 2 (Burwell et al., 1977). Alberts and Spomer (1985) resampled the loess profiles of Watersheds 1 and 2 to a 15-m depth in 1984, and identified a prominent increase in $\text{NO}_3\text{-N}$ centered at a 10.7-m depth in Watershed 1, where a concentration of $16 \text{ mg NO}_3\text{-N kg}^{-1}$ soil contrasted the 3 mg kg^{-1} found at 15 m. The watersheds received similar N applications from 1964 to 1968 and from 1975 to 1995 (Table 1). Karlen et al. (1999) listed annual N applications from 1964 to 1995. Corn grain harvest rarely accounted for more than 110 kg ha^{-1} of N removal (Karlen et al., 1998).

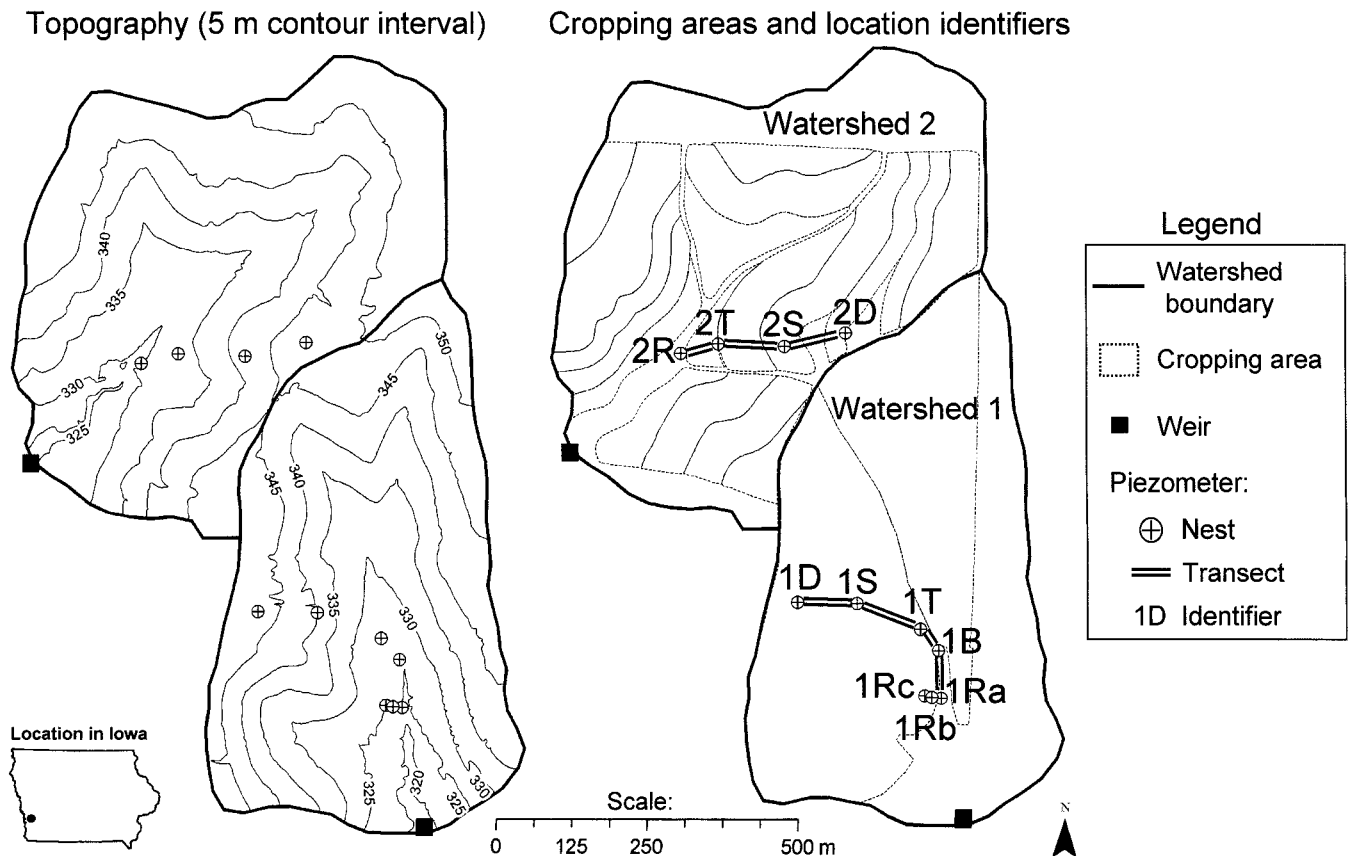


Fig. 1. Maps of Watersheds 1 and 2 of the Deep Loess Research Station (DLRS), showing topography (left) and cropping boundaries (right). Topographic contours (left map) are at a 5-m interval and labeled as meters above sea level. Locations of piezometer nests and weirs are shown in both maps; the right map also identifies the nests and shows piezometer transect locations. Table 1 names the piezometer transects and gives depths of the installations at each piezometer nest.

New crop rotations were established in both watersheds beginning in 1996 (Table 1). Watershed 1 was placed under a corn–soybean [*Glycine max* (L.) Merr.] rotation, with each crop covering either the eastern or western half of the watershed every year (Fig. 1). Watershed 2 was placed under a six-year rotation of corn, soybean, and corn, followed by three years of alfalfa (*Medicago sativa* L.). The six-year rotation was implemented in narrow contour strips (Fig. 1), with all six years of the rotation always present (about 1/3 in corn, 1/6 in soybean, and 1/2 in alfalfa with all three stand ages represented). With both rotations, only the corn received N fertilizer, which was on an alternate-year basis in Watershed 1, and two out of six years in Watershed 2. After the new rotations were established, N fertilizer rates applied to corn from 1996 to 2001 aver-

aged 151 kg N ha⁻¹ in Watershed 1 and 117 kg N ha⁻¹ in Watershed 2. The fertilizer N applications are determined using soil testing; larger carryover of legume-fixed N and differences in timing of soil tests may have contributed to smaller rates being recommended in Watershed 2.

The change in farming practices since 1996 is hypothesized to cause a difference between the two catchments in ground water and stream-baseflow NO₃-N concentrations. One question that has arisen, however, is whether the effect of the excessive nitrogen fertilizations between 1969 and 1974 has persisted in ground water. Thus, to discern the effects of recent management changes, we must determine if current NO₃-N concentrations in ground water and baseflow in Watershed 1

Table 1. A summary of crop rotations and fertilizer applications during different periods of research in Deep Loess Research Station (DLRS) Watersheds 1 and 2.

Time period	Watershed 1			Watershed 2		
	Crop rotation†	Mean N application	Crop area fertilized	Crop rotation†	Mean N application	Crop area fertilized
		kg N ha ⁻¹ yr ⁻¹	%		kg N ha ⁻¹ yr ⁻¹	%
1964–1968	CC	150	100	CC	150	100
1969–1974	CC	446	100	CC	172	100
1975–1995	CC	186	100	CC	186	100
1996–2002	CS	151	50	CSCA3	117	33

† CC, continuous corn; CS, corn–soybean; CSCA3, corn–soybean–corn–three years of alfalfa.

could still be influenced by these large N applications that date back about 30 years.

METHODS

Three independent lines of evidence were constructed to identify ground water ages, travel times, and patterns of ground water recharge, and discern the effects of past and present management on $\text{NO}_3\text{-N}$ concentrations in the two watersheds. These lines of evidence were based on hydrologic measurements, spatial trends in isotope chemistry, and spatial and temporal trends in $\text{NO}_3\text{-N}$ concentrations in waters and deep sediments.

Monitoring Installations

In each watershed, a transect of four piezometer nests was installed in 1996, at divide (D), mid-slope (S), toe-slope (T), and riparian valley (R) positions. The nests are identified by watershed number and landscape position (e.g., 1D, 2S; see Fig. 1). In 1999, three additional riparian-zone piezometer nests were installed in Watershed 1, including 1B, and two nests installed near 1R, denoted 1Rb and 1Rc (the 1996-installed 1R nest was denoted 1Ra; see Fig. 1). The 1999 installations were a part of separate research on a riparian buffer planted in Watershed 1 during 2000. Piezometer nests comprise three transects, including two long transects identified by watershed (e.g., W1, W2), and a short riparian transect in Watershed 1 identified as W1_{rip} (Table 2). Each transect portrays an expected path of ground water flow based on field interpretation of the terrain.

During drilling, cores were taken to the depth at which glacial till was encountered, by a drill rig with a hollow-stem auger. The till defined the depth of drilling because it provides an underlying aquitard to ground water within the deep loess. Cores were subsampled, wrapped, and chilled for later analysis of bulk density (Blake and Hartge, 1986), organic C, total N, and $\text{NO}_3\text{-N}$. Organic C and total N were determined by dry combustion, while $\text{NO}_3\text{-N}$ was determined by an autoanalyzer technique on 2 M KCl extractions (Cambardella et al., 1994).

Materials encountered during coring were recorded with depth, which at upland (D and S) positions included Peoria and Pisgah loess of Wisconsinian age, underlain by Loveland loess of Illinoian age, and then pre-Illinoian till. Sand lenses were common at the till-loess interface. Buried paleosols known as Farmdale, Sangamon, and Yarmouth soils occurred at the upper surface of the Pisgah, Loveland, and till units, respectively. The stratigraphy and paleosols of the Loess Hills are described by Prior (1991), Ruhe (1969), and Kay and Graham (1943). In the riparian valleys, alluvial deposits com-

posed of reworked loess were described following a scheme proposed by Bettis (1990). A 50-mm-i.d. piezometer was then set just above the till, with a 0.6-m-long screen. Additional boreholes were also drilled to install shallower piezometers (Table 2) at depths above and below the Sangamon paleosol (a possible impedance to vertical water flow), and/or at the observed depth of the water table (i.e., where water-saturated sediments were first encountered). One or two suction-cup lysimeters were also installed above the saturated zone at several locations (Table 2). Installations at each landscape position were located within a few meters of one another, usually in line along the topographic contour. Piezometers were gravel-packed to at least 0.2 m above the screened interval and grouted to the land surface with bentonite. Lysimeters were similarly installed but were set in a silica-flour slurry to provide hydraulic contact between the ceramic cup and the surrounding unsaturated sediments. Steel casings were set to cover the polyvinyl chloride (PVC) plastic piezometers and lysimeters. Map coordinates and elevations of all piezometers were determined by a global positioning system (GPS) survey with relative errors of 0.01 m in horizontal and vertical dimensions.

Hydrologic Measurements

The hydraulic conductivity (K_s) of the saturated zone was measured by conducting slug tests in each piezometer. A solid PVC rod was lowered and later raised to conduct slug-down and slug-up tests. Hydraulic head was measured during each slug test using a pressure transducer and data logging system. The slug test data were analyzed using the Hvorslev (1951) method. At each piezometer, K_s was taken as the mean of the values measured by rising and falling head. The K_s data were sorted by type of deposit (till, sand at the till interface, loess, and alluvium), and the geometric mean was calculated for each unit. For several of the deep piezometers completed in till or its Yarmouth paleosol, measurements of K_s were not made because there was no response in the water levels after slug addition. Water levels were measured in each piezometer on a monthly basis.

Positional survey data, coring descriptions, water levels, and hydraulic conductivities were used to estimate times required for ground water to travel along the three transects. The saturated zone dominantly occurred within the Loveland loess above the toeslopes, and in alluvium below. Given the uniformity and common origin of these two deposits, the ground water flow system is simple in its hydrogeology, and simple calculations were used to evaluate lateral flow along these transects. Hydraulic gradients and conductivities were used to

Table 2. Summary of monitoring transects, with numbers and depths of suction-cup lysimeters and piezometers at each piezometer nest location.

Transect†	Piezometer nest†	Number of lysimeters	Depths of lysimeters	Number of piezometers	Depths of piezometers‡
			m		m
W2	2D	2	(6), (12)	3	(17), (22), (28)
W2	2S	2	6, 9	3	13, 16, (21)
W2	2T	1	5.5	3	4.5, 14, (17)
W2	2R	0	—	4	3, 6, 9, 12
W1	1D	2	(6), 12	3	21, (23), 27
W1	1S	2	8, 11	3	14.5, 16.5, (21)
W1	1T	1	3	3	5, 14, (16)
W1	1B	0	—	3	4, 7, 9
W1 & W1 _{rip}	1Ra	0	—	4	5, 9, 14, 16
W1 _{rip}	1Rb	0	—	3	3.5, 6, 8.5
W1 _{rip}	1Rc	0	—	3	4.5, 8, 11.5

† Drilling locations are indicated in Fig. 1.

‡ Depths enclosed by parentheses indicate that poor water yield prevented consistent monthly sampling. Depths indicated in italic type (30 total) indicate piezometers sampled for isotopic analyses.

determine ground water velocities using the Darcy equation. Survey data and water levels were used to calculate hydraulic gradients for June 2001 and April 2002, which were the months with the highest and lowest average water levels since the second set of piezometers was installed in 1999. The average head of all piezometers at each nest was calculated for both times. Hydraulic gradients were calculated by taking the difference in average head between adjacent nests, divided by the distance between them. The geometric mean K_s calculated for the loess and alluvium deposits was then used to calculate flow velocities. The flow rates were next divided by an estimated effective porosity of $0.2 \text{ m}^3 \text{ m}^{-3}$ to calculate ground water velocities, which were finally divided into the distances between transect locations and summed to obtain an estimated travel time along each transect. The effective porosity was estimated to be about half of the average porosity of $0.42 \text{ m}^3 \text{ m}^{-3}$, which was estimated from bulk densities of cores collected during piezometer installation. This was deemed an appropriate value to estimate the travel of a solute's center of mass. Also, water contents of the loess soils at 1500 kPa, near a 1-m depth, are about $0.20 \text{ m}^3 \text{ m}^{-3}$ (Rob Malone, personal communication, 2003), suggesting that little flow occurs in about half the pore space.

Isotope Chemistry

Input Record for Tritium in Precipitation

A record of annual tritium activities in precipitation was constructed to represent past concentrations of tritium that have recharged ground water at the site. We obtained tritium units (TU) data for annual precipitation published by the International Atomic Energy Agency (1992), which covered the period from 1953 through 1986, and monthly data from the Global Network for Isotopes in Precipitation database (International Atomic Energy Agency and World Meteorological Organization, 2001) from 1987 through 1999. Annual weighted averages were calculated from the latter source. Records from three monitoring stations were used to compile a continuous tritium input record from 1953 to 1999. A station at Lincoln, Nebraska, located 90 km southwest of these watersheds, was operated from 1962 to 1986 and provided a data record considered to be local for those years. Annual TU values before 1962 and after 1986 were estimated based on relationships between records at Lincoln and St. Louis, Missouri, which covered from 1987 to 1993, and between records at Lincoln and Ottawa, ON, Canada, to estimate from 1953 through 1961 and from 1994 through 1999 (Table 3). These relationships were calculated using a power function:

$$Y = aX^b \quad [1]$$

in which X is the distant (St. Louis or Ottawa) station's and Y is the local (Lincoln) station's TU data. The coefficients a and b were fit by an iterative technique because of the small number of data points. Subset periods of common record were selected (Table 3) to avoid obvious bias that occurred when values from peak years of tritium fallout were included. The complete TU record at Lincoln ranged across nearly three orders of magnitude. Restricting the input data provided a curve fit and root mean square error (RMSE) that represented the numeric range to be estimated (Table 3). To be explicit, the peak years of 1963–1964 were excluded in estimating the pre-1962 record, and only the last 11 years of common record were used to estimate the post-1987 record, so that estimated values were not, in effect, extrapolated from observations during peak fallout.

The post-1986 TU precipitation record was also estimated in a second way that relied only on local data. This method also employed Eq. [1], with the same Y variate, but the X variate was the number of years since 1962. Additional local data points were available for the years of 1992 and 2001. Simpkins (1995) measured the tritium activity at Ames, Iowa, to be 11.02 TU during 1992 (weighted average). This was considered local data because Ames is only about 200 km from the study area. The 2001 TU value was obtained from an on-site sample, collected in June, and combined from four 1.8-m-deep lysimeters located near the divide between the two watersheds, in the area between Piezometer Nests 1D and 2D. This sample's 7.1 TU was assumed to indicate the tritium activity of precipitation during the previous six months. Using these local data, a power function was fit to obtain a curve from 1963 to 2001, giving the result shown in the last row of Table 3. Most of the gross (real space, rather than log space) error associated with this model occurred for the first year of peak fallout, and so the RMSE is reported as 11%. Once these precipitation records were constructed, the expected tritium activity of each year's precipitation in 2001 was calculated based on a 12.43-year half-life.

Isotope Sampling and Analyses

Between 13 and 15 June 2001, 33 water samples were collected for isotopic analyses of $\delta^{18}\text{O}$, $\delta^2\text{D}$, and ^3T (TU). The samples were taken from 30 piezometers (Table 2) and from the stream baseflow passing the weir of each watershed, plus the combined sample from four 1.8-m-depth lysimeters described above. The isotope analyses were conducted at the University of Waterloo Environmental Isotope Laboratory using methods described by Coleman et al. (1982) and Drimmie et al. (1991) for deuterium, Epstein and Maeda (1953) for ^{18}O , and Drimmie et al. (1993) and Taylor (1977) for enriched tritium. Tritium results had a detection limit of 0.8

Table 3. Summary of regressions used to complete an estimated annual input record for tritium in precipitation. Data are from International Atomic Energy Agency (1992), International Atomic Energy Agency and World Meteorological Organization (2001), and Simpkins (1995). Selection of input data is discussed in the text.

Years of missing record estimated†	Location and years of record available	Years of record selected as input data	$a \ddagger$	$b \ddagger$	r^2	RMSE§
1953–1961	Ottawa, ON; 1953–1999	1962, 1965–1986	0.30	1.18	0.98	TU 21.7
1987–1993	St. Louis, MO; 1963–1993	1975–1986	0.83	1.15	0.91	4.1
1994–1999	Ottawa, ON; 1953–1999	1975–1986	0.05	1.64	0.85	6.0
1987–1991, 1993–2000	local trend with time; 1962–1986, 1992, 2001	all except 1962	4448	–1.71	0.97	11%¶

† Missing values before 1962 and after 1986 were estimated. Post-1986 estimates were based on relationships with two other stations (Rows 2 and 3), and on interpolation of a local trend over time (Row 4).

‡ Coefficients a and b are defined by Eq. [1].

§ Root mean square error, as tritium units (TU).

¶ The RMSE is reported as a percent in this instance because the Y data (local TU values) span three orders of magnitude.

Table 4. A summary of hydraulic conductivity data from slug tests on piezometers in Watersheds 1 and 2. Data were sorted by type of deposit and include results from additional riparian-valley piezometers in Watershed 1 not mapped in Fig. 1.

Type of deposit	Hydraulic conductivity		<i>n</i>
	Range	Geometric mean	
	m s^{-1}		
Till	2.8×10^{-5} to 2.7×10^{-8}	1.4×10^{-6}	13
Sand (till interface)	3.8×10^{-5} to 2.1×10^{-6}	6.5×10^{-6}	6
Loess	8.9×10^{-5} to 1.4×10^{-7}	1.0×10^{-5}	11
Alluvium	1.6×10^{-4} to 1.0×10^{-8}	4.1×10^{-6}	26

TU, and analytical errors that varied from 0.5 to 1.4 TU and increased with tritium activity. Isotope samples were submitted in three sets to spread the incurred financial costs, and turnaround times from the lab varied depending on its workload. Consequently, the samples were analyzed either 90, 120, or 321 d after collection, corresponding to 0.020, 0.026, or 0.071 fractional half lives of tritium (12.43 yr), respectively. Accordingly, tritium values were back-corrected from the date of analysis to the sampling date. While these were minor corrections, ranging from 0.0 to 0.7 TU, they did account for known errors and were greater than half the analytical error in four of the last-analyzed samples.

Stable isotope data, expressed as $\delta^2\text{D}\text{‰}$ and $\delta^{18}\text{O}\text{‰}$, were plotted and a local meteoric water line (LMWL) was estimated using the reduced major axis method (Mann, 1987). This regression method was applied to stable isotope data by the International Atomic Energy Agency (1992), but was named orthogonal regression in that document. The method was chosen because it reduces slope attenuation that can be important when the range of observations is limited and the *X* variate is subject to measurement error.

A single index was calculated to indicate the isotopic enrichment or depletion of any single sample relative to others at the site, by scaling all the $\delta^2\text{D}$ and $\delta^{18}\text{O}\text{‰}$ values between -1 and 0 (values were all negative), and then adding one to their sum. This scaled the data between maximum and minimum possible values of 1 and -1 , with positive values being relatively enriched, negative values relatively depleted, and near-zero values close to a mean isotopic condition for the site. This index facilitated simple graphics to evaluate spatial patterns of the isotopic data, which were confirmed by *t* tests on the original isotope values, assuming equal variances.

Nutrients in Water and Deep-Core Sediments

Upon completion, the installations were sampled on a monthly basis; water samples from lysimeters and piezometers were analyzed for $\text{NO}_3\text{-N}$ concentration using an autoanalyzer technique with a 1.0 mg L^{-1} detection limit that is described by Hatfield et al. (1999). At least 1.5 water-column volumes were purged from each piezometer before sampling. Recharge to several deep piezometers was too slow to allow this purging, and sampling of these installations (identified in Table 2) was done either less frequently (e.g., twice per year), or, where water levels did not recover within a month of sampling (e.g., at Nest 2D), was suspended. Stream baseflow was also sampled at the outlet of both watersheds for $\text{NO}_3\text{-N}$, on a monthly basis from autumn 1996 through summer 2000, and then on a weekly basis after spring 2001. Baseflow concentrations between the two watersheds were compared by a paired *t* test, under the null hypothesis that there was no difference in $\text{NO}_3\text{-N}$ concentrations.

RESULTS AND DISCUSSION

Ground Water Flow

Results of slug tests across all piezometers (Table 4) showed that small K_s values were most common in till, whereas the alluvium showed the most variation in K_s . Mean K_s values are within the range expected for unconsolidated sediments derived from loess or till (Fetter, 2001).

Hydraulic heads (Fig. 2) were used to determine gradients in vertical and horizontal directions. There were

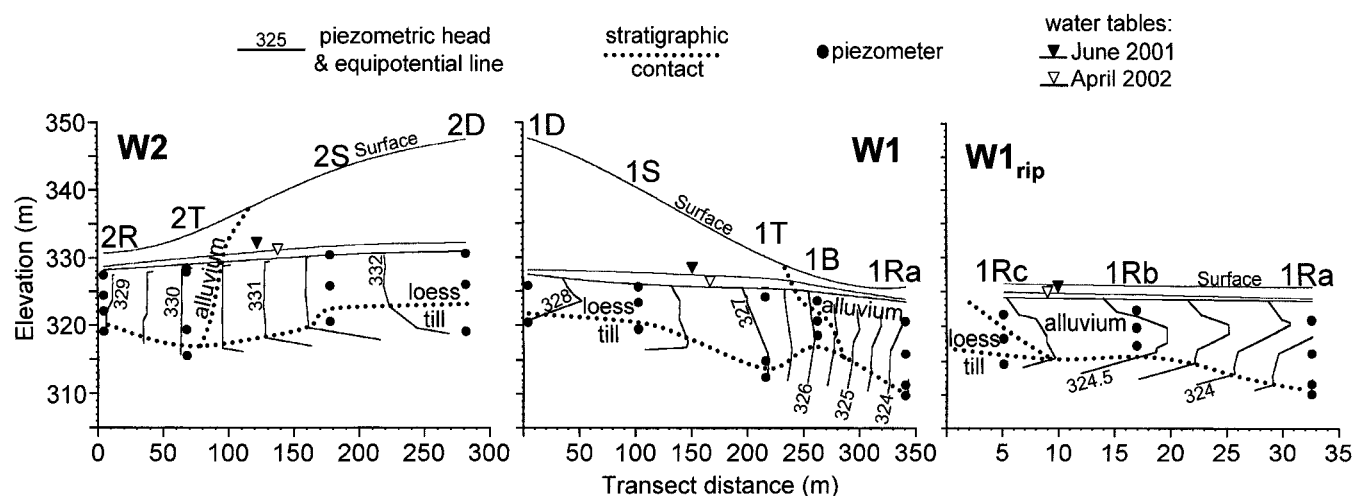


Fig. 2. Cross-sections of hydraulic heads (given as meters of elevation) along the three transects (W2, W1, and W1_{rip}), interpolated from June 2001 water level measurements. Contour intervals are 0.5 m of head in the left and center cross-sections, and 0.25 m of head in the right cross-section. The identifier for each piezometer nest is indicated along the land surface. Stratigraphic contacts between major deposits (till, loess, and alluvium) are indicated by thick dotted lines. Refer to Fig. 1 and Table 2 for piezometer-nest and cross-section locations and identifiers.

persistent vertical gradients within most piezometer nests, but no evidence that buried paleosols had a major influence on ground water flow. Downward gradients ($>0.02 \text{ m m}^{-1}$) occurred between the two deepest piezometers at the divide position in both watersheds. The largest downward gradient (approximately 0.08 m m^{-1}) occurred between the two upper most piezometers at Position 1Ra, indicating a zone of slow permeability between these two screen depths. There were consistent upward gradients between the upper two piezometers at Positions 1S, 1T, 1B, and 1Rc, but these were usually small ($<0.02 \text{ m m}^{-1}$). Larger upward gradients occurred between the middle two piezometers at Position 2R (between 0.02 and 0.04 m m^{-1}) and between the upper two piezometers at Position 1Rb (approximately 0.08 m m^{-1}). A constriction caused by a shallow depth of the till contact could contribute to these upward gradients (Fig. 2). Several vertical gradients are evident in the cross-sections of Fig. 2. A reversal in vertical gradient along the W1_{rip} transect, from upward at 1Rb to downward at 1Ra, suggests heterogeneities in the alluvial deposits.

Lateral flow gradients between adjacent transect positions were calculated from the difference in average hydraulic heads at each nest. Gradients were usually small above the toeslope positions (0.003 – 0.015 m m^{-1}) in both watersheds, but larger below the toeslopes (0.012 – 0.042 m m^{-1}). This difference is also evident in the cross-sections of Fig. 2.

Estimates of ground water velocity between piezometer nests averaged 13.5 m yr^{-1} , and varied from 5.3 to 27.1 m yr^{-1} . The estimates are based on a mean K_s (Table 4) applied for flow through loess above the toeslopes and through alluvium below the toeslopes. Estimated travel times (Table 5) varied according to the length of each transect and changes in hydraulic gradients. Along the W2 transect, larger gradients occurred with higher water levels measured in June 2001. But along W1, the larger gradients occurred during April 2002. Between 64 and 82% of the travel times occurred above the toeslope positions. Because vertical and horizontal gradients are both present, actual travel distances of ground water may be greater than horizontal distances and travel times are considered conservative. Results therefore suggest that land management effects on ground water could persist for decades in these watersheds (Table 5).

Isotope Chemistry

Precipitation Tritium Record

There was good agreement between the two constructs of the post-1986 record of tritium in local precipi-

Table 5. Transect lengths and estimated ground water travel times for transects.

Transect†	Length m	Travel time for water levels measured	
		June 2001	April 2002
W2	277	22.7	25.9
W1	337	36.1	31.0
W1 _{rip}	28	1.4	2.5

† Locations are shown in Fig. 1.

tation (i.e., estimates based on International Atomic Energy Agency stations and on local trend). Agreement between the St. Louis–estimated and the local trend–estimated data between 1987 and 1993 was excellent, because there was a close tracking between the St. Louis and Lincoln records from peak bomb fallout until data collection at Lincoln ceased in 1986. Also, the estimated tritium activity for local precipitation in 1992 was 13.37 TU using the St. Louis record, and was 12.61 TU based on the local trend. Simpkins (1995) estimated a value of 12.68 TU for Lincoln in 1992, based on a relationship with St. Louis data determined by a slightly different method. Local-trend estimates of post-1993 tritium were larger than those estimated using Ottawa data (Fig. 3), but the differences do not affect data interpretation.

Isotopic decay was calculated for the local estimates of mean annual tritium activities in precipitation, using both constructs of the post-1986 record, to obtain the expected residual tritium activity in 2001 (Fig. 3). Sub-surface and baseflow waters that fell as precipitation within 20 years before sampling cannot be differentiated. However, values exceeding 10 to 12 TU suggest the presence of waters aged between 20 and 40 years, at least in mixture. Very small tritium values (i.e., <3 TU) would suggest waters predominantly of “pre-bomb” origin, or at least 45 years old.

Tritium in Ground Water

After correction for varying sampling-analysis time lags, tritium activities ranged from 0.8 to 18.5 TU. Small tritium activities (<3 TU), indicating water predating any research at the site, occurred in 6 of the 33 samples and were always in the deepest ground water (Fig. 4). Tritium values exceeding 12 TU, showing an influence of 20- to 40-yr-old precipitation, occurred in 9 of the 33

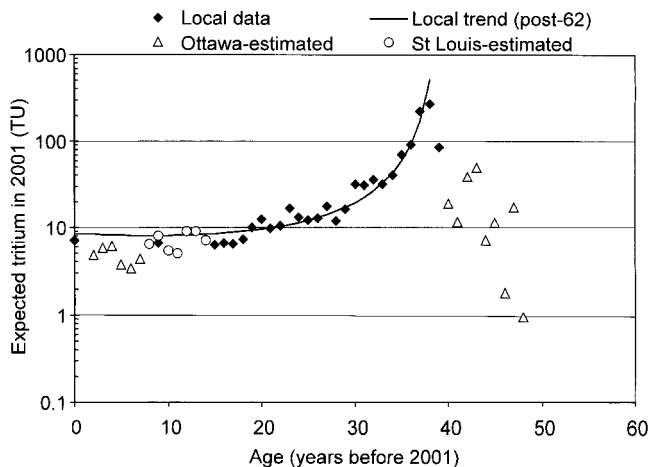


Fig. 3. Expected residual tritium activities in 2001 for water originating as local annual precipitation between 1953 and 2001. Isotopic decay based on a 12.43-yr half-life was applied to a constructed tritium record to obtain this plot. The constructed record included local data (from Lincoln, NE; Ames, IA; and on-site), a trend in the local data, and estimates for missing years based on records from St. Louis, MO and Ottawa, ON, Canada, as specified in Table 3. Precipitation data are from International Atomic Energy Agency (1992), International Atomic Energy Agency and World Meteorological Organization (2001), and Simpkins (1995).

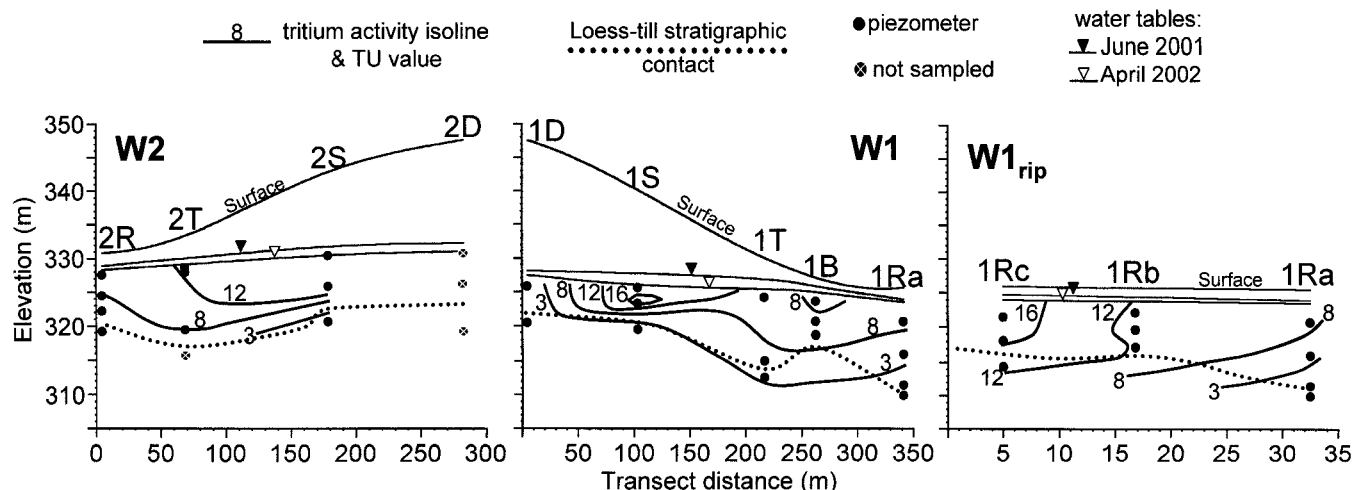


Fig. 4. Cross-sections showing variations in ground water tritium activity (TU) along three transects (W2, W1, and W1_{rip}) during June 2001. Tritium contours are interpreted as pre-1953 in age for waters with tritium activity of <3 TU, whereas values of >12 TU show an influence of “bomb-peak” precipitation between 1963 and 1980. Intermediate values indicate recent or mixed-age waters. Piezometers not sampled for tritium are indicated by a crossed symbol. Piezometer-nest identifiers are shown along the land surface. Refer to Fig. 1 and Table 2 for piezometer-nest and cross-section locations and identifiers.

samples. These larger tritium activities always occurred below midslope (1S, 2S) and toeslope (shallow at 2T, 1Rc) positions (Fig. 4). Values of intermediate tritium activity (4–12 TU) were most frequent below riparian and toeslope positions (1T, 1B, 1Ra, 1Rb, deep at 2T, 2R), indicating recent or mixed-age waters. Samples collected from the weirs had tritium activities of 11.1 and 12.5 TU for Watersheds 1 and 2, respectively, which are not dissimilar given analytical errors near 1.0 TU. The baseflow samples would be considered of mixed origin, with possibly a weak influence of 20- to 40-yr-old waters, and were consistent with TU values from the shallowest riparian-valley piezometers.

Stable Isotopes

Stable isotope concentrations ranged from -5.6 to -8.9‰ for $\delta^{18}\text{O}$ and from -39.6 to -60.9‰ for $\delta^2\text{H}$. Ground water contains a mix of waters from multiple precipitation events, and therefore the range of data was smaller than is typically observed in precipitation samples. When the data were fit to estimate a local meteoric water line (Fig. 5), the limited range resulted in a fairly low precision ($r^2 = 0.72$) and the local meteoric water line (LMWL) was not statistically different from the global meteoric water line (GMWL), or other LMWL published from the region (Harvey and Welker, 2000; International Atomic Energy Agency, 1992; Matheney and Gerla, 1996; Simpkins, 1995). The average $\delta^{18}\text{O}$ was -7.1‰ and the average $\delta^2\text{H}$ was -49.2‰ . While some evaporative enrichment of ground water relative to local precipitation could occur (Gonfiantini et al., 1998), these averages are similar to those published for precipitation at Ames, IA (Simpkins, 1995) and Chicago, IL (International Atomic Energy Agency, 1992). The International Atomic Energy Agency did not monitor these stable isotopes at Lincoln, NE, or St. Louis, MO. There are data from central Nebraska (Harvey and Welker, 2000) showing isotopic depletion

in precipitation relative to Ames and Chicago, probably resulting from less influence of moisture from the Gulf of Mexico (Simpkins, 1995; Harvey and Welker, 2000). The central Nebraska site is more than 400 km west of the Deep Loess Research Station, across a steep transition in climate and native vegetation from semi-arid short-grass prairie (west) to humid tall-grass prairie (east).

There was a distinct spatial pattern to the stable isotope data despite their small range in variation (Fig. 6). Ground water beneath the upper landscape positions (D and S) was isotopically enriched compared with toeslope (T) or riparian valley (R) positions ($p < 0.01$), whether the stable isotope data were tested individually or combined on a single scale between -1 and $+1$. Differences were significant, albeit small, with $\delta^{18}\text{O}$ averaging -6.4‰ in upper landscape positions, -7.1‰ at the toeslope positions, and -7.5‰ in the riparian positions, and

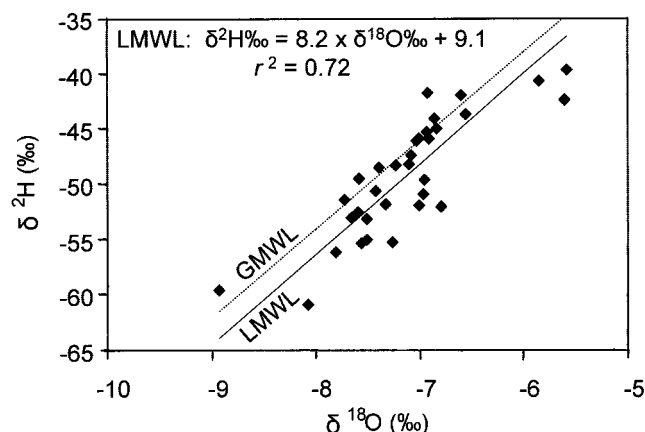


Fig. 5. Plot of stable isotope data ($\delta^{18}\text{O}\text{‰}$ versus $\delta^2\text{H}\text{‰}$) from 33 water samples collected in Watersheds 1 and 2. A local meteoric water line (LMWL) fit to the data (solid line) has an r^2 of 0.72. The global meteoric water line (GMWL; dotted line) is also plotted as a reference.

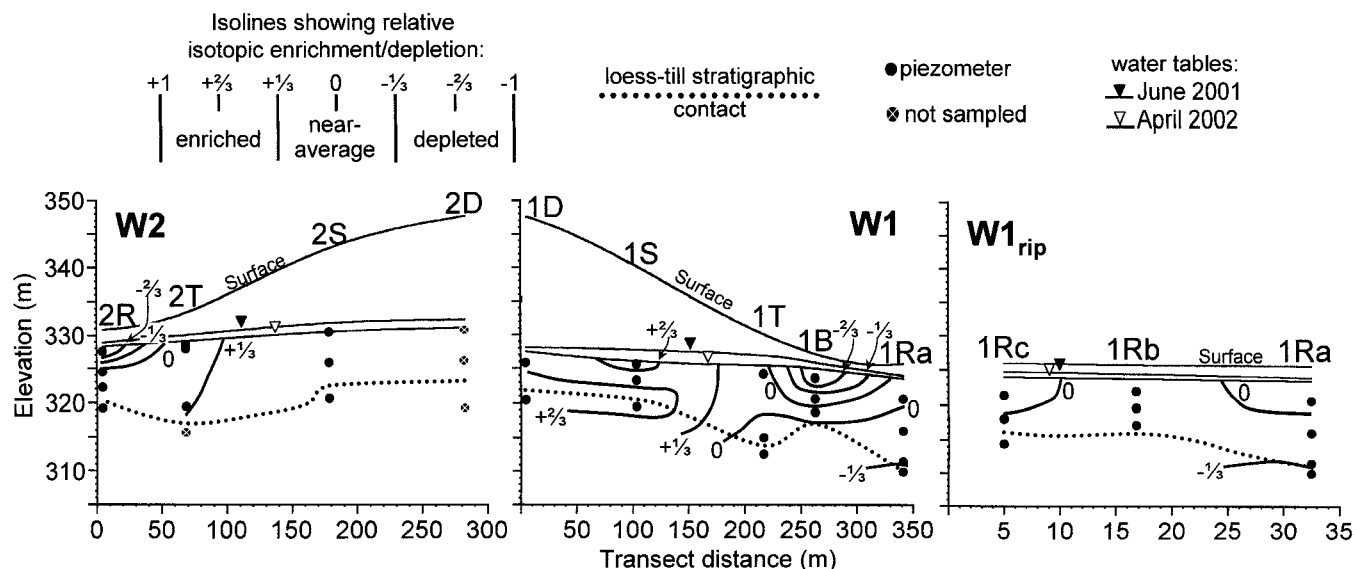


Fig. 6. Cross-sections showing variations in relative isotopic enrichment or depletion, using a combined scale of $\delta^{18}\text{O}_{\text{‰}}$ and $\delta^2\text{H}_{\text{‰}}$, in ground water along three transects (W2, W1, W1_{rip}) in Watersheds 1 and 2. Piezometers not sampled for stable isotopes are indicated by a crossed symbol. Piezometer-nest identifiers are shown along the land surface. Refer to Fig. 1 and Table 2 for piezometer-nest and cross-section locations and identifiers.

$\delta^2\text{H}$ averaging -42.4‰ in upper landscape positions, -50.4‰ at the toeslope positions, and -52.6‰ in the riparian positions. Also, classification of the data by landscape position accounted for 52% of the variance in the $\delta^{18}\text{O}$ data and 60% of the variance in the $\delta^2\text{H}$ data, based on a single-factor analysis of variance. This indicates there are differences in processes or sources affecting ground water according to landscape position. Three possible mechanisms causing this difference are upward movement of deep ground water, seasonal infiltration patterns, and landscape differences in water vapor transport in soil.

First, upward movement of deep ground water could be occurring at lower landscape positions. Older, deep ground water might be depleted. While this was reported for deep waters of glacial origin in Wisconsin (Simpkins and Bradbury, 1992) and North Dakota (Matheney and Gerla, 1996), it has not been reported this far south of recent (i.e., Wisconsinan) glaciation. There was no obvious depletion in piezometers below the till contact. In fact, the most depleted waters were found in the shallowest ground water at Positions 2R and 1B. Thus, upward flow from the till aquitard is not suspected.

A second and more likely possibility is that seasonal changes in runoff and infiltration act to segregate recharge waters. Snowmelt and cold spring rains are isotopically depleted, and occur when there is little plant cover. These depleted waters would be most prone to runoff from upper slopes and then infiltrate near the toeslope. Winds can also redistribute snow toward lower landscape positions. Warmer summer rains, on the other hand, would be enriched and occur when there is crop cover that increases interception, infiltration, and transpiration, and reduces runoff. Also, rain occurring during small precipitation events is likely to infiltrate where it falls, and this rain could, on average, be enriched by

the “amount effect.” That is, falling raindrops become more enriched by evaporation during small events than during large events, because the atmosphere is likely to be saturated with water vapor during large events (Ingraham, 1998).

A third potential cause could be related to movement of water vapor under winter conditions. Loess soils are known to exhibit frost heave, which results from upward movement of water vapor from depth toward frozen surface soils. Vapor movement through soil is known to be fractionating (Barnes and Turner, 1998), and in frozen soils would lead to enrichment of the deeper soil water. In the lower landscape position, the water table would provide a shallow lower boundary for this process, and therefore upon melt the depleted soil ice would readily remix with the originating water. In the uplands, however, the process occurs under drier conditions with no fixed lower boundary. Complete remixing of melted soil ice to depth would not occur as readily and deeper soil water that recharges ground water could remain enriched. Such a phenomenon has not been documented, but is plausible.

In sum, seasonal runoff and infiltration mechanisms are thought to be most responsible for the relative enrichment of ground water below upland positions and depletion in ground water below the toeslopes (Fig. 6). Large relative depletion in the shallowest piezometers at Positions 2R and 1B further support this. Processes of soil freezing and thawing may also contribute to the observed pattern.

Nitrate Nitrogen Concentrations

Deep Sediments

A large increase in sediment $\text{NO}_3\text{-N}$ concentrations (mg kg^{-1}) was observed in the deep cores taken during

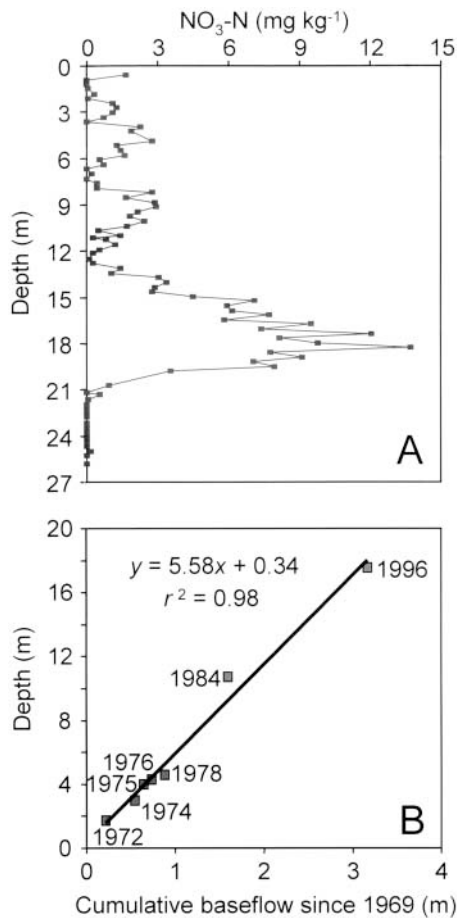


Fig. 7. (A) Nitrate N concentrations with depth in soils and deep sediments at Position 1D (Fig. 1), from core samples taken in 1996. (B) Depths of maximum NO₃-N concentrations measured in 1972, 1974–1976, 1978, 1984 (Alberts and Spomer, 1985; Schuman et al., 1975), and 1996, plotted against cumulative baseflow from Watershed 1 since 1969.

1996 at Position 1D (Fig. 7), centered near the 17.5-m depth. This pattern was not observed in any of the other deep cores, and only 25 individual samples out of 323 collected at the other coring positions showed NO₃-N concentrations exceeding 4 mg kg⁻¹. Total N and C data from these cores did not indicate this NO₃-N could originate from the sediments or buried paleosols (i.e., 1D and 2D showed similar carbon contents that decreased similarly with depth). If this NO₃-N resulted from large N fertilizer applications between 1969 and 1974, then there would be some consistency with historical data on sediment NO₃-N collected in 1972, 1974–1976, 1978, and 1984 (Schuman et al., 1975; Alberts et al., 1977; Alberts and Spomer, 1985). Depths of increased NO₃-N in sediments reported for each of these years showed consistent downward movement. These depths were plotted against the cumulative amounts of water that percolated through these watersheds since 1969 to each year of sampling (Fig. 7). Baseflow provides a surrogate measure of this percolation, and was taken from stream discharge records separated into runoff and baseflow components (Kramer et al., 1999). The result (Fig. 7) showed a strong linear relationship ($r^2 = 0.98$)

between depths of increased NO₃-N and cumulative baseflow, showing the consistent movement of a pulse of NO₃-N through the deep unsaturated zone since the first experiment, in response to hydrologic fluxes through the watershed's subsurface. If the baseflow resulted from deep percolation that occurred at spatially uniform rates, then this relationship suggests that 1 m of deep percolation caused NO₃-N to percolate about 5.6 m through the unsaturated zone. This ratio leads to an estimated "mobile" water content of about 0.18 m³ m⁻³. This is about the difference between the average volumetric water content found during bulk density determinations on the deep cores (0.37 m³ m⁻³) and estimated 1500 kPa water contents (about 0.20 m³ m⁻³ at a 1-m depth), and therefore seems reasonable. A similar relationship with time suggests that the excess NO₃-N percolated through this 20-m unsaturated zone at an average annual rate of 0.67 m yr⁻¹ ($r^2 = 0.99$; data not shown). These relationships provide a third line of evidence that some of the N from large fertilizer applications between 1969 and 1974 resided in the subsurface of Watershed 1 until 1996. Given the inferred rate of movement of this NO₃-N pulse to depth, one would anticipate that this NO₃-N would have percolated into the saturated zone before 1996 at lower landscape positions. This would explain why large sediment concentrations were not observed at depth at lower W1 positions.

The total NO₃-N storage in the 20-m-deep sediments at 1D was 930 kg ha⁻¹, about two-thirds of which was below 15 m. The deep profile at 2D, in contrast, showed about 629 kg NO₃-N ha⁻¹ to a 20-m depth, with 60% of this mass found within the top 10 m and only 6% below 15 m. A 15-m-depth sampling in 1984 (Alberts and Spomer, 1985) found 1910 kg ha⁻¹ in Watershed 1, and 1060 kg ha⁻¹ in Watershed 2. The other profiles from our 1996 coring showed between 110 and 490 kg NO₃-N ha⁻¹, which varied according to the unsaturated zone's thickness. In a third Deep Loess Research Station watershed, Steinheimer and Scoggin (1998) estimated that about 1200 kg N ha⁻¹ could have accumulated in the deep loess between 1972 and 1990, under continuous corn with N applications averaging 167 kg ha⁻¹ yr⁻¹.

Ground Water

The largest concentrations of NO₃-N in water were found within the deep suction-cup lysimeters installed in upland positions (Fig. 8). The smallest concentrations occurred in the deepest ground water. Concentrations in the saturated zone decreased not only with depth, but also with distance downslope. This could result from an increasing effect of denitrification with residence time, increased carbon availability and denitrification rates in alluvial sediments, and/or dilution from greater infiltration of runoff waters near the toeslope position, which bear small NO₃-N concentrations. These hypotheses are the subject of ongoing research at this site.

While NO₃-N concentrations commonly decreased with increasing depth, the vertical changes in NO₃-N concentrations were inconsistent below the toeslopes

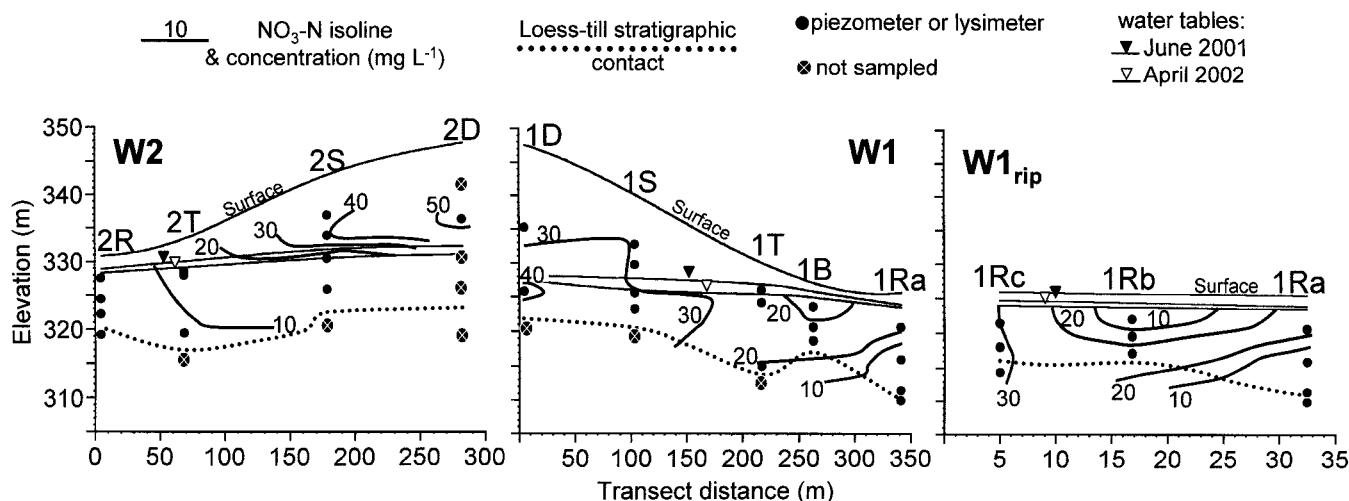


Fig. 8. Cross-sections showing variations in $\text{NO}_3\text{-N}$ concentrations in water from piezometers and deep lysimeters along three transects (W2, W1, W1_{rip}) as measured in June 2001. Lysimeters are indicated by filled circles located above the water table, whereas piezometers are located below the water table. Installations not sampled for nitrate are indicated by a crossed symbol. Piezometer-nest identifiers are shown along the land surface. Refer to Fig. 1 and Table 2 for piezometer-nest and cross-section locations and identifiers.

(Fig. 8). Similar concentrations with depth occurred at Positions 2R and 1Rc, although there was greater temporal variation in the upper piezometer at 2R. Also, at Positions 1B and 1Rb, concentrations increased at depth (Fig. 8) due to dilution by recharge water and/or denitrification of upward-moving water. Depleted isotopic conditions suggest recharge occurred at Position 1B, while upward hydraulic gradients occurred at both locations and were larger at 1Rb. At 1Ra, there were larger concentrations in the shallowest piezometer, compared with often nondetectable concentrations in deeper ground water (Fig. 9). A large downward vertical gradient occurs at this position and the deeper waters are dominantly pre-1950s in age (Fig. 4).

Temporal changes have also occurred in $\text{NO}_3\text{-N}$ concentrations in ground water and lysimeter waters during monitoring (Fig. 9). In particular, the record at 1D shows that a large pulse of $\text{NO}_3\text{-N}$ in the deep sediments (Fig. 7) entered the water table and caused $\text{NO}_3\text{-N}$ concentrations to peak during the year 2000. The timing of these changes in concentration is consistent with the expected movement of this pulse of $\text{NO}_3\text{-N}$ from the sediment into ground water, as the relationship with baseflow (Fig. 7) would support entry into ground water during 1999, given baseflow volumes of 144 mm in 1997, 238 mm in 1998, and 321 mm in 1999 (Larry Kramer, personal communication, 2003). But, the $\text{NO}_3\text{-N}$ contributing water has little apparent effect on tritium in the upper piezometer (Fig. 5), where a dominant “pre-bomb” age would be inferred from 2.8 TU.

Large changes in $\text{NO}_3\text{-N}$ concentrations have occurred in upland (S and D) positions, particularly in the lysimeters in both watersheds (i.e., 6- and 12-m depths at 2D, 6- and 9-m depths at 2S, 12 m at 1D, and 11 m at 1S; see Fig. 9). These variations in the lysimeter waters are not well explained by profiles of $\text{NO}_3\text{-N}$ in core samples, and are asynchronous among each other and with ground water recharge events that caused increased water levels in early 1998 and 1999. Temporal changes in

mineralization of organic matter and unsaturated water contents may contribute to the patterns. There are unpublished data that indicate large decreases in soil organic matter occurred in the surface soils of these watersheds during the past 30 years (Tom Moorman, personal communication, 2002). Piezometers in Watershed 1 also showed significant temporal variation in $\text{NO}_3\text{-N}$ (i.e., 21-m depth at 1D; 14.5- and 16.5-m depth at 1S), including the recent entry of a large pulse of deep $\text{NO}_3\text{-N}$ to ground water at 1D. Note that piezometers at 2D were not sampled due to low sampling yield and slow recovery (>30 d) of water levels after sample withdrawal.

In the R and T positions, $\text{NO}_3\text{-N}$ concentrations in ground water are smaller and most stable in Watershed 2, with slow increases evident in Watershed 1 (Fig. 9). The larger $\text{NO}_3\text{-N}$ concentrations in Watershed 1 are reflected in the baseflow concentrations measured at the watershed outlet weirs (Fig. 10), which averaged 20 mg L^{-1} in Watershed 1 and 12 mg L^{-1} in Watershed 2. A paired *t* test showed this difference to be significant ($p < 0.01$). Given Watershed 1's average annual baseflow of 131 mm between 1975 and 2001, each 10 mg L^{-1} of $\text{NO}_3\text{-N}$ would equate to 13.1 $\text{kg N ha}^{-1} \text{ yr}^{-1}$ exported in baseflow. Therefore, very large concentrations would be needed over a prolonged period to export an additional 1656 kg N ha^{-1} (i.e., the excess amount of N applied to Watershed 1 from 1969 to 1974).

CONCLUSIONS

Three independent lines of evidence support the conclusion that ground water concentrations of $\text{NO}_3\text{-N}$ in Watershed 1 are still influenced by large amounts of fertilizer N applied 30 years ago. Ground water time-of-travel estimates and tritium data both suggest that ground water remains resident in these watersheds for decades. Given such residence times, the differences in $\text{NO}_3\text{-N}$ concentrations between these two watersheds could easily be the result of an experiment conducted

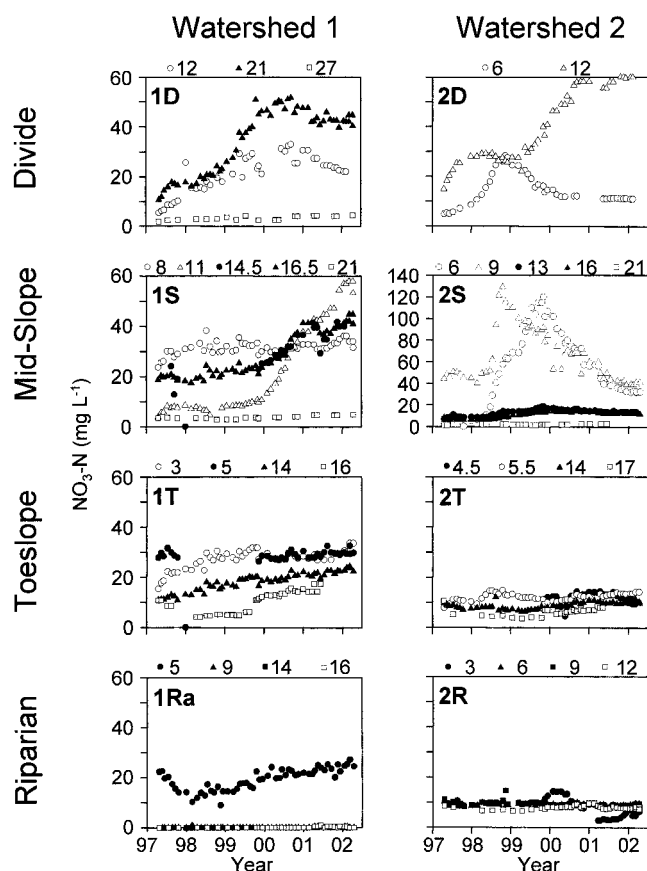


Fig. 9. Temporal changes in $\text{NO}_3\text{-N}$ concentrations in water collected from lysimeters and piezometers at D, S, T, and R positions in Watersheds 1 and 2 (see Fig. 1). Open symbols denote suction-cup lysimeters, black-filled symbols denote piezometers in loess, and gray-filled symbols denote piezometers near the till contact. Depths of monitoring (meters below surface) are noted above each plot. Nondetectable concentrations ($<1 \text{ mg L}^{-1}$) are plotted at zero. Symbols overlap in some plots. Some installations did not yield water samples every month (see Table 2).

between 1969 and 1974. Furthermore, analyses of $\text{NO}_3\text{-N}$ in deep sediments, considered with historical data, indicate that a pulse of soil $\text{NO}_3\text{-N}$ has percolated through the deep unsaturated zone since 1969, in response to subsurface hydrologic fluxes (baseflow) through the watershed. Recent increases in ground water $\text{NO}_3\text{-N}$ concentrations near the watershed divide were consistent with this sediment- $\text{NO}_3\text{-N}$ record and its relationship with annual baseflow. These three lines of evidence, when taken together, suggest that heavy fertilizer applications between 1969 and 1974 continue to influence $\text{NO}_3\text{-N}$ concentrations in ground water within Watershed 1.

Isotopic data suggest that ground water recharge in these watersheds may frequently occur by infiltration of runoff water at lower landscape positions. Results of stable isotope analyses (Fig. 6) suggest that runoff from colder rains infiltrates at and below toeslope positions. Tritium data (Fig. 4) also support recent and/or mixed origin waters at these landscape positions.

Concentrations of $\text{NO}_3\text{-N}$ in ground water beneath upslope positions in Watershed 1 are still influenced by an experiment conducted from 1969 to 1974. However,

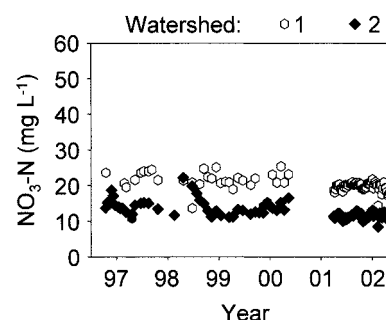


Fig. 10. Nitrate N concentrations in baseflow collected at the outlet weirs of Watersheds 1 and 2.

in lower landscape positions, runoff from upslope infiltrates and mixes into ground water, and therefore historical and recent land use practices affect current $\text{NO}_3\text{-N}$ concentrations. Travel times across the riparian zone are estimated at around two or three years. But, due partly to focused recharge below the toeslope, it appears that upslope ground water is being contributed to the riparian areas very slowly. Overall, it will be difficult to clearly discern the effect of recent cropping system changes between these two watersheds by monitoring ground water or baseflow for many years. Therefore, shallow monitoring of unsaturated-zone waters may be the most reliable means to examine effects of crop rotation on water quality. Ongoing research will assess the denitrification of ground water beneath this site's riparian zone.

In conclusion, multiple lines of evidence gathered in these small watersheds suggest it takes at least several decades for subsurface water to travel from the divide to the stream. In many watersheds, changes in agricultural practices may take several decades to fully effect improvements in ground water quality.

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